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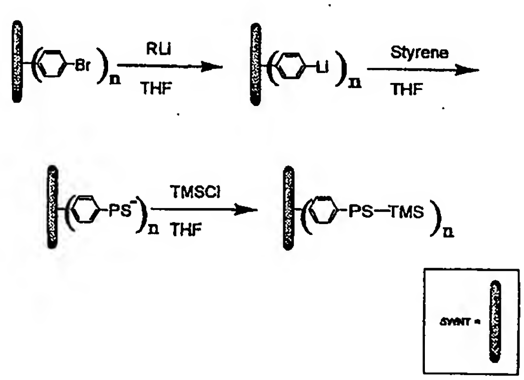
(54) Title: POLYMERIZATION INITIATED AT THE SIDEWALLS OF CARBON NANOTUBES



(57) Abstract: The present invention is directed to aryl halide (such as aryl bromide) functionalized carbon nanotubes can be utilized in anionic polymerization processes to form polymer-carbon nanotube materials with improved dispersion ability in polymer matrices. In this process the aryl halide is reacted with an alkyllithium species or is reacted with a metal to replace the aryl-bromine bond with an aryl-lithium or aryl-metal bond, respectively. It has further been discovered that other functionalized carbon nanotubes, after deprotonation with a deprotonation agent, can similarly be utilized in anionic polymerization processes to form polymer-carbon nanotube materials. Additionally or alternatively, a ring opening polymerization process can be performed. The resultant materials can be used by themselves due to their enhanced strength and reinforcement ability when compared to their unbound polymer analogs. Additionally, these materials can also be blended with pre-formed polymers to establish compatibility and enhanced dispersion of nanotubes in otherwise hard to disperse matrices resulting in significantly improved material properties. The resultant polymer-carbon nanotube materials can also be used in drug delivery processes due to their improved dispersion ability and biodegradability, and can also be used for scaffolding to promote cellular growth of tissue.

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POLYMERIZATION INITIATED AT THE SIDEWALLS OF CARBON NANOTUBES

[0001] This invention was made with support from the National Aeronautics and Space Administration, Grant Nos. NASA-JSC-NCC-9-77 and TEES 68371, passed through from NASA-URETI NCC-01-0203; the National Science Foundation, Grant No. NSR-DMR-0073046; and the U.S. Air Force Office of Scientific Research, Grant No. F49620-01-0364.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This Application claims priority to United States Provisional Patent Application Serial No. 60/480,348 filed June 20, 2003.

FIELD OF THE INVENTION

[0003] The present invention relates generally to processes for growing polymer chains via anionic polymerization, and/or alternatively via ring opening polymerization, from the sidewalls of functionalized carbon nanotubes, which will facilitate greater dispersion in polymer matrices and greatly enhanced reinforcement ability in polymeric material.

BACKGROUND

[0004] Fullerenes are closed-cage molecules composed entirely of sp^2-hybridized carbons, arranged in hexagons and pentagons. Fullerenes (*e.g.*, C_{60}) were first identified as closed spheroidal cages produced by condensation from vaporized carbon. Fullerene tubes are produced in carbon deposits on the cathode in carbon arc methods of producing spheroidal fullerenes from vaporized carbon. Ebbesen *et al.*, Nature, 1992, 358:220 and Ebbesen *et al.*, Annual Review of Materials Science, 1994, 24:235-264. Such tubes are referred to herein as carbon nanotubes. Many of the carbon nanotubes made by these processes were multi-wall nanotubes (MWNTs), *i.e.*, the carbon nanotubes resembled concentric cylinders having multiple walls or shells arranged in a manner which can be considered analogous to Russian "nesting dolls." Carbon nanotubes having up to seven walls have been described in

presence of a variety of functional groups bound to the nanotubes, such as single-wall carbon nanotubes, for sensing applications. And once blended, some applications may benefit from the thermal removal of these chemical moieties, as described in PCT publication WO 02/060812 by Tour *et al.*, filed January 29, 2002 and incorporated by reference herein.

[0007] While there have been many reports and review articles on the production and physical properties of carbon nanotubes, reports on chemical manipulation of nanotubes have been slow to emerge. There have been reports of functionalizing nanotube ends with carboxylic groups (Rao, *et al.*, *Chem. Commun.*, 1996,1525-1526; Wong, *et al.*, *Nature*, 1998, 394:52-55), and then further manipulation to tether them to gold particles via thiol linkages (Liu, *et al.*, *Science*, 1998, 280:1253-1256). Haddon and co-workers (Chen, *et al.*, *Science*, 1998, 282:95-98) have reported solvating single-wall carbon nanotubes by adding octadecylamine groups on the ends of the tubes and then adding dichlorocarbenes to the nanotube sidewall, albeit in relatively low quantities (~2%).

[0008] Success at covalent sidewall derivatization of single-wall carbon nanotubes has been limited in scope, and the reactivity of the sidewalls has been compared to the reactivity of the basal plane of graphite. Aihara, *J. Phys. Chem.* 1994, 98:9773-9776. A viable route to direct sidewall functionalization of single-wall carbon nanotubes has been fluorination at elevated temperatures, which process was disclosed in a patent commonly assigned to the assignee of the present Application, United States Patent No. 6,645,455, "Chemical Derivatization Of Single-Wall Carbon Nanotubes To Facilitate Solvation Thereof; And Use Of Derivatized Nanotubes To Form Catalyst-Containing Seed Materials For Use In Making Carbon Fibers," to Margrave *et al.*, issued November 11, 2003. These functionalized nanotubes may either be de-fluorinated by treatment with hydrazine or allowed to react with strong nucleophiles, such as alkyllithium reagents. Although fluorinated nanotubes may well provide access to a variety of functionalized materials, the two-step protocol and functional group intolerance to organolithium reagents may render such processes incompatible with certain, ultimate uses of the carbon nanotubes. Other attempts at sidewall modification have been hampered by the presence of significant graphitic or amorphous carbon contaminants. Chen, Y. *et al.*, *J. Mater Res.* 1998, 13:2423-2431. For some reviews on sidewall functionalization,

The functional group attached to the nanotube would be a chemically active part of the polymerization, which would result in a composite material in which the nanotubes are chemically involved.

SUMMARY

[0012] It has been discovered that aryl halide (such as aryl bromide) functionalized carbon nanotubes can be utilized in anionic polymerization processes to form polymer-carbon nanotube materials with improved dispersion ability in polymer matrices. In this process the aryl halide is reacted with an alkyllithium species or is reacted with a metal to replace the aryl-bromine bond with an aryl-lithium or aryl-metal bond, respectively. It has further been discovered that other functionalized carbon nanotubes, after deprotonation with a deprotonation agent, can similarly be utilized in anionic polymerization processes to form polymer-carbon nanotube materials. Additionally or alternatively, a ring opening polymerization process can be performed. The resultant materials can be used by themselves due to their enhanced strength and reinforcement ability when compared to their unbound polymer analogs. Additionally, these materials can also be blended with pre-formed polymers to establish compatibility and enhanced dispersion of nanotubes in otherwise hard to disperse matrices resulting in significantly improved material properties. The resultant polymer-carbon nanotube materials can also be used in drug delivery processes due to their improved dispersion ability and biodegradability, and can also be used for scaffolding to promote cellular growth of tissue.

[0013] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

Alternatively, the carbon nanotubes can be functionalized with other aryl halides bonded to the sidewalls. Further alternatively, the carbon nanotubes can be functionalized with a species having nucleation sites for the polymerization, such as species having carbon, sulfur, oxygen, and nitrogen sites for polymerization.

[0022] As reflected in FIGURE 1, aryl bromide functionalized nanotubes can be dispersed in a solvent with an alkyllithium species (RLi), which can be, for example, provided as a tetrahydrofuran solution of *n*-butyllithium. The concentration of the solution can be in the range between about 0.1 and 1.0 mg/ml. The nanotube material may then be allowed to settle and the excess n-butyllithium solution optionally may be removed via canulation. The remaining nanotube material may be washed, such as with three portions of dry tetrahydrofuran, to thoroughly remove any residual n-butyllithium. The nanotube material may then be dispersed in a solvent, such as dry tetrahydrofuran.

[0023] After dispersion, a monomer, such as, for example, stryrene is added to the reaction vessel. Other monomers can be utilized, such as those selected from the group consisting of styrene, acrylates, methyl acrylates, vinyl acetate, vinyl pyridines, isoprene (such as 1,4-isoprene), butadiene (such as 1,3-butadiene, 2-methyl-1,3-butadiene, 2-methyl-1,4-butadiene), chloroprene, acrylonitrile, maleic anhydride, and combinations thereof. The concentration of the monomer is in the range between about 0.03 and 0.16 g/ml The temperature at polymerization is typically in the range between about 0 and 50°C

[0024] An anionic polymerization process is employed utilizing the functionalized carbon nanotubes and the monomer, wherein the polymerization can be effected by an anionic initiator.

[0025] Upon completion of the anionic polymerization, the active chain ends can be terminated with an appropriate terminating agent, such as ethanol, acetaldehyde, trimethylsilyl chloride, or combinations thereof. The average chain length of the polymer bonded to the carbon nanotubes are generally in the range between about 5 and about 1 million, and can more specifically be in the range between about 1000 and about 1 million. After termination, the reaction mixture may be diluted and filtered to remove any large particulate. The filtrate can then be concentrated under

reinforcement properties. For instance nanocomposites thus synthesized using 1,3-butadiene can be saturated to form tethered analogs of low density polyethylene that form miscible mixtures with high density polyethylene resulting in nanocomposites where nanotubes are dispersed in a HDPE matrix with superior material properties. Similarly, starting from 1,4-isoprene followed by saturation will lead to the formation of a strictly alternating copolymer of ethylene and propylene that is compatible with many commercial grades of ethylene – propylene elastomers. Additionally, preparation of high vinyl butadiene based polymers by polymerization in a highly polar solvent will lead to the tethering of copolymers of 1,4 – 1,2 polybutadienes with high 1,2 content resulting in compatibility with isotactic, syndiotactic and atactic polypropylenes.

[0030] Some embodiments of the present invention involve a ring opening polymerization utilizing a ring opening polymerization initiator. For instance, ring opening polymerization of ε-caprolactone is initiated by a number of different types of catalysts utilizing various co-initiators such as alcohols, carboxylic acids or amines. Mechanisms for the polymerization of PCL are presented in Figures 4(a)-(c). Polymerization of ε-caprolactone proceeds by anionic (4(a)), cationic (4(b)), or a coordination insertion type mechanism (4(c)) [Storey and Sherman,"Kinetics and Mechanism of the Stannous Octoate-Catalyzed Bulk Polymerization of epsilon-caprolactone", Macromolecules, 2002, 35, 1504-1512]. Depending on experimental conditions and reagents used, it is understood that that all three mechanisms may possibly occur simultaneously. In the present Application, it is further understood that the alcohol or acid functionality covalently bound to the SWNT can thus act as nucleophile (via the conjugate base, as in Figure 4(a)) or can participate in forming the alkoxide that initiates the polymerization as in Figure 4(c). Polymerizations were conducted under several experimental conditions: (i) in bulk at 130°C utilizing a tin octoate based catalyst [Storey and Sherman, "Kinetics and Mechanism of the Stannous Octoate-Catalyzed Bulk Polymerization of epsilon-caprolactone", Macromolecules, 2002, 35, 1504-1512] and either hydroxyl terminus or carboxylic acid terminus functionalized nanotubes (see FIGURES 5(b) and 5(a), respectively), (ii) in solution with toluene as the solvent at 100°C utilizing a tin octoate based catalyst [Kowalski;Duda and Penczek, "Kinetics and mechanism of cyclic esters polymerization initiated with tin(II) octoate, 1", Macromol. Rapid Commun. 19, 1998,

However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments that are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1

[0034] This Example illustrates the growth of a polymer chain from the sidewalls of functionalized SWNTs in accordance with embodiments of the present invention.

[0035] Aryl bromide functionalized single wall carbon nanotubes (0.015 g, 0.022 mmol Br) are dispersed in THF (5 mL) and a solution of *n*-butyllithium (5 mL, 2.19 M in hexane) was added at 23°C and the solution was allowed to stir for 10 min. The stirring was then turned off and the nanotubes were allowed to settle out of solution. After settling, the excess *n*-butyllithium solution was removed from the reaction vessel via cannula and the nanotubes were washed 3 times with dry THF (10 mL) to remove unreacted *n*-butyllithium.

[0036] The flask was then charged with dry THF (10 mL) and the tubes were dispersed in solution with rapid stirring. Styrene (1.7 mL, 15 mmol) was added to the reaction vessel and the mixture was stirred for 180 min before adding ethanol (1 mL) or a function terminator of choice such as trimethylsilyl chloride. The mixture was then diluted with 100 mL dichloromethane and filtered through Fisherbrand P8 filter paper to remove any large particulate. The filtrate was concentrated under reduced pressure and precipitated into methanol. The resulting gray powder (product) was then collected by filtration, using Whatman 41 filter paper and dried under vacuum (0.1 mm) to a constant weight (typically, 0.100-1.00 g depending on the precise amount of styrene added).

Example 2

[0037] This Example illustrates the growth of a polymer chain from the sidewalls of functionalized SWNTs via a ring opening polymerization process in accordance with embodiments of the present invention.

WHAT IS CLAIMED IS:

1. A method comprising:

a) providing functionalized carbon nanotubes, wherein the functionalized carbon nanotubes comprise a functionalized species on the sidewall of the carbon nanotubes selected from the group consisting of (i) aryl halide functionalized carbon nanotubes and (ii) specie comprising a nucleation site operable for anionic or ring opening polymerization;

b) dispersing said aryl halide functionalized carbon nanotubes in a solvent;

c) adding to the solvent at least one of: (i) an alkyllithium species, wherein the alkylthium species reacts with the aryl halide functionalized carbon nanotubes (ii) a metal, wherein the metal reacts with the aryl halide functionalized carbon nanotubes and replaces aryl-halide bonds with aryl-metal bonds, (iii) a deprotonating agent, wherein the deprotonating agent deprotonates the nucleation sites of the functionalized carbon nanotubes and form initiator groups for the anionic or ring opening polymerization;

d) adding a monomer to the solvent; and

e) initiating anionic or ring opening polymerization utilizing the monomer and the functionalized carbon nanotubes to form a polymer-carbon nanotube material.

2. A method comprising:

a) providing aryl halide functionalized carbon nanotubes;

b) dispersing said aryl halide functionalized carbon nanotubes in a solvent;

c) adding an alkyllithium species to the solvent, wherein the alkylthium species reacts with the aryl halide functionalized carbon nanotubes;

d) adding a monomer to the solvent; and

e) initiating anionic or ring opening polymerization utilizing the monomer and the functionalized carbon nanotubes to form a polymer-carbon nanotube material.

b) dispersing the functionalized carbon nanotubes in a solvent;
c) adding a deprotonating agent to the solvent, wherein the deprotonating agent deprotonate the nucleation sites of the functionalized carbon nanotubes and form initiator groups for the anionic or ring opening polymerization;
d) adding a monomer to the solvent; and
e) initiating anionic or ring opening polymerization utilizing the monomer and the functionalized carbon nanotubes to form a polymer-carbon nanotube material.

11. The method of Claim 10, wherein the nucleation sites of the functionalized carbon nanotubes are at least one of the elements selected from group consisting of carbon, sulfur, oxygen, and nitrogen.

12. The method of Claim 10, wherein the functionalized carbon nanotubes are selected from the group consisting of phenol functionalized carbon nanotubes, thiophenol functionalized carbon nanotubes, phenethyl alcohol functionalized nanotubes (CNT-C_6H_4-CH_2CH_2OH), CNT-C_6H_4-NHBoc, and combinations thereof.

13. The method of Claims 10-11 or 12, wherein the species functionalized on the carbon nanotubes is functionalized on the sidewall of the carbon nanotubes

14. The method of Claims 10-11 or 12, wherein the deprotonating agent comprises a base.

15. The method of Claim 14, wherein the base is selected from the group consisting of KOH, KH, NaOH, NaH, and potassium hexamethyldisilazide.

16. The method of Claims 10-11 or 12, wherein the deprotonating agent comprises a metal operable for deprotonating the nucleation sites.

27. The methods of Claims 1-5, 10-11 or 12, wherein concentration of the monomer is in the range between about 0.03 and about 0. 16 g/ml.

28. The methods of Claims 1-5, 10-11 or 12, wherein the step of initiating anionic polymerization occurs at a temperature in the range between about 0°C and about 50°C.

29. The methods of Claims 1-5, 10-11 or 12, wherein average chain length of the polymer bonded the carbon nanotubes in the polymer-carbon nanotube material is in the range between about 5 and about 1 million,

30. The method of Claim 29, wherein the average chain length is between about 1000 and about 1 million.

31. The methods of Claims 1-5, 10-11 or 12, wherein a catalyst is used during the step of initiating anionic or ring opening polymerization.

32. The method of Claim 31, wherein the catalyst comprises $TiCl_4$.

33. The method of Claims 1-5, 10-11 or 12 further comprising the step of utilizing the polymer-carbon nanotube material in a drug delivery process.

34. The method of Claims 1-5, 10-11 or 12, further comprising the step of utilizing the polymer-carbon nanotube material for scaffolding to promote cellular tissue growth.

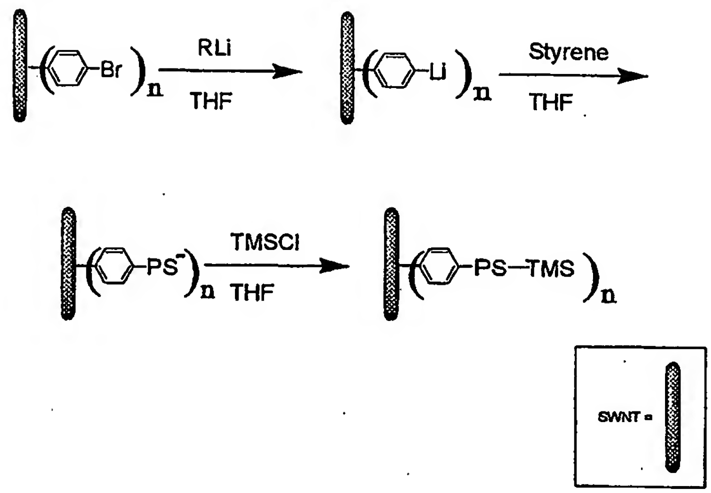


Fig. 1

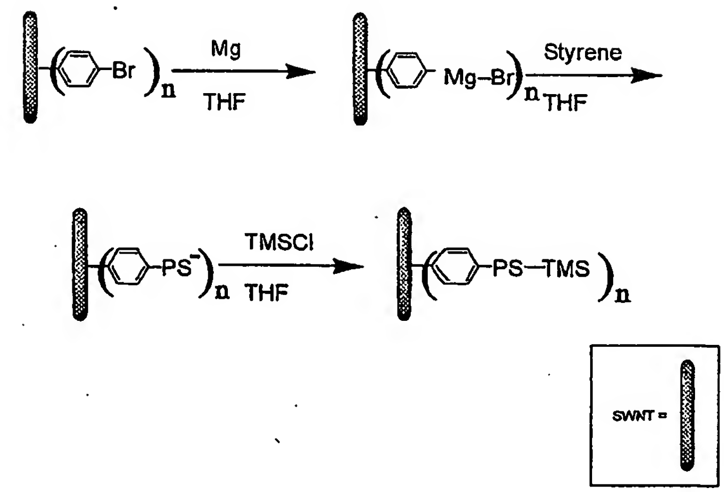


Fig. 2

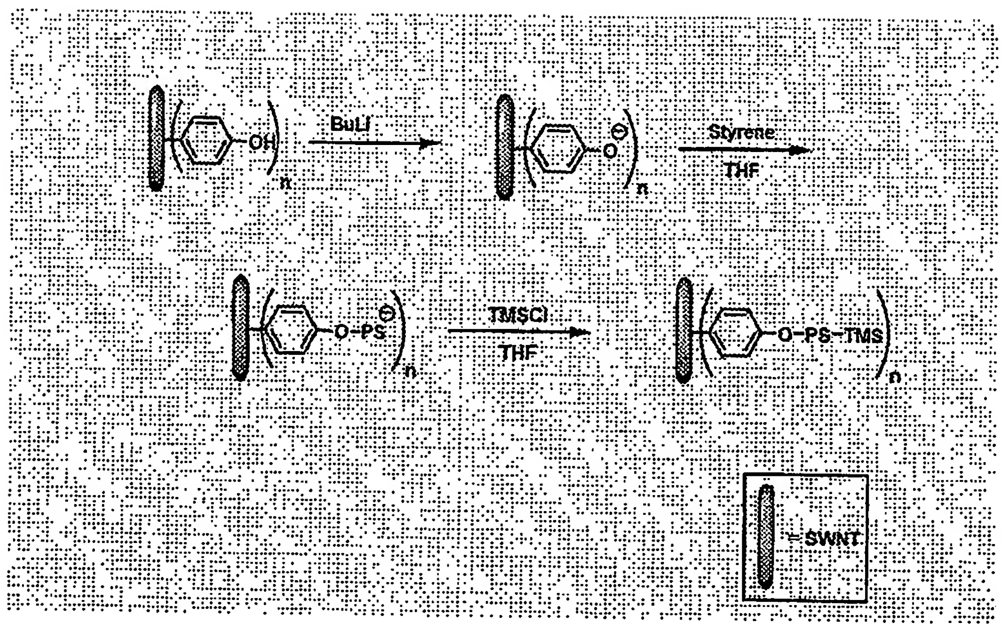


Fig. 3

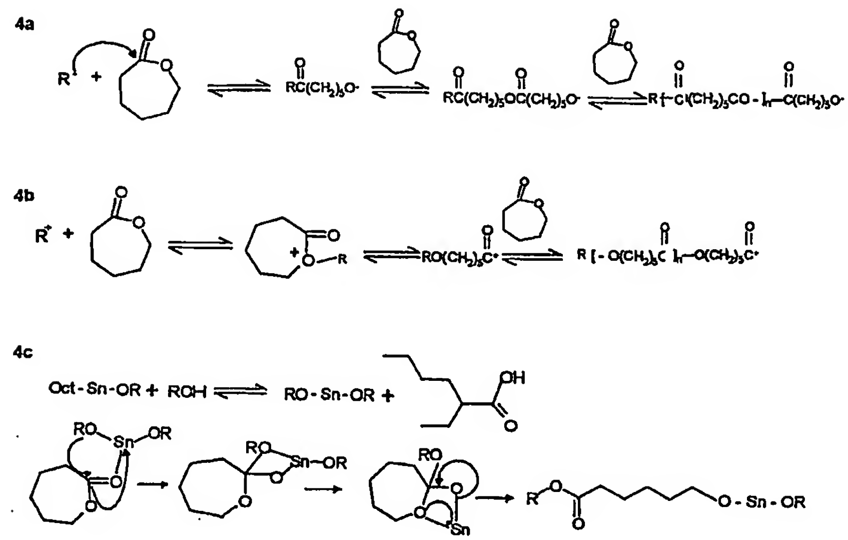
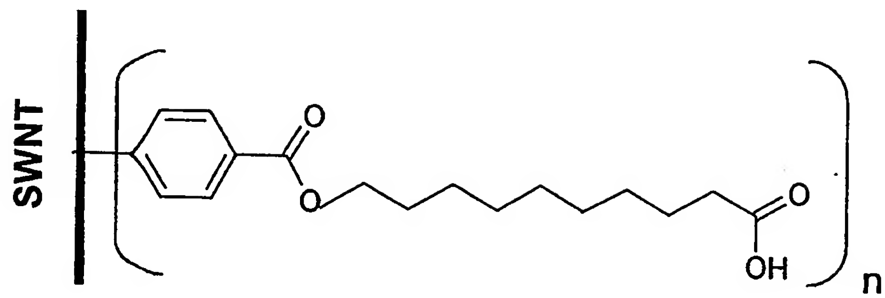


Fig. 4

5a



5b

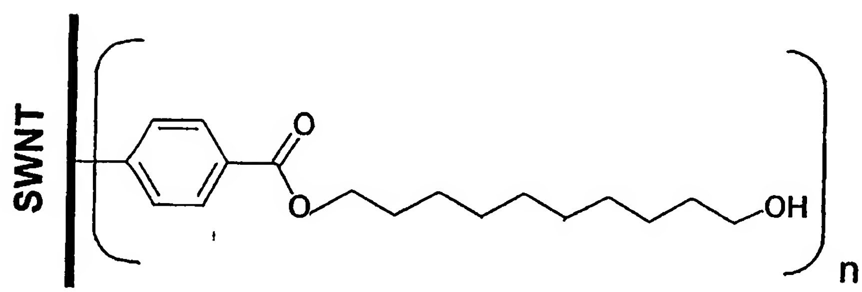


Fig. 5